Iminophosphanes: Synthesis and Coordination Chemistry

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2017

document version
Publisher's PDF, also known as Version of record

Nitrilium Ions: Synthesis and Applications

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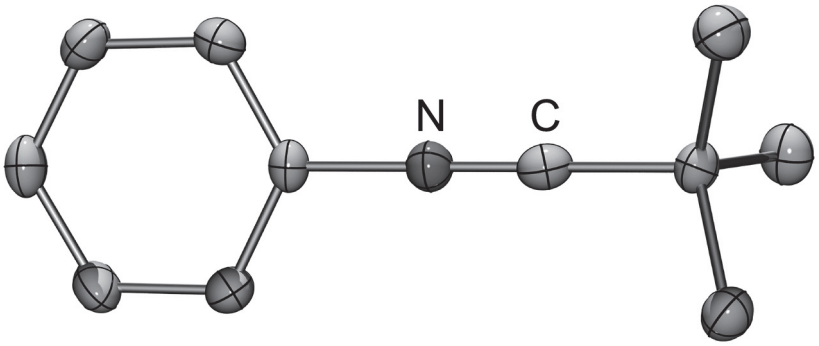


Abstract: This review will give an overview of the generation and properties of nitrilium ions and their application in synthesis. Despite their high reactivity various stable nitrilium ions are accessible through various methods that will be discussed herein. Both stable nitrilium ions and *in situ* generated nitrilium ions can be used for the synthesis of a wide range of unsaturated nitrogen containing heterocycles typically by forming the heterocycle upon intramolecular electrophilic attack on the nitrilium- or iminium carbon of the formed intermediate. Furthermore, this review will show the potential of nitrilium ions as highly suitable imine synthons that react with a wide variety of nucleophiles.

1.1. Introduction

Nitrilium ions **1** are since long known as *reactive intermediates* in valuable organic transformations like the Beckman rearrangement and the Ritter, von Braun, and Bischer-Napieralski reactions, while Meerwein and others reported on *stable nitrilium salts* already half a century ago. This duality of *reactivity versus stability* is ideal to fully exploit the synthetic potential of such a simple synthon, but this is not quite what has happened in the past decades. Whereas much has been accomplished, illustrated by two earlier reviews,[1] nitrilium ions are now being rediscovered because of their versatile reactivity, which is addressed in this review. By first sketching the historical perspective of nitrilium ions it becomes abundantly clear that this important synthon has tremendous synthetic value beyond its current boundaries.

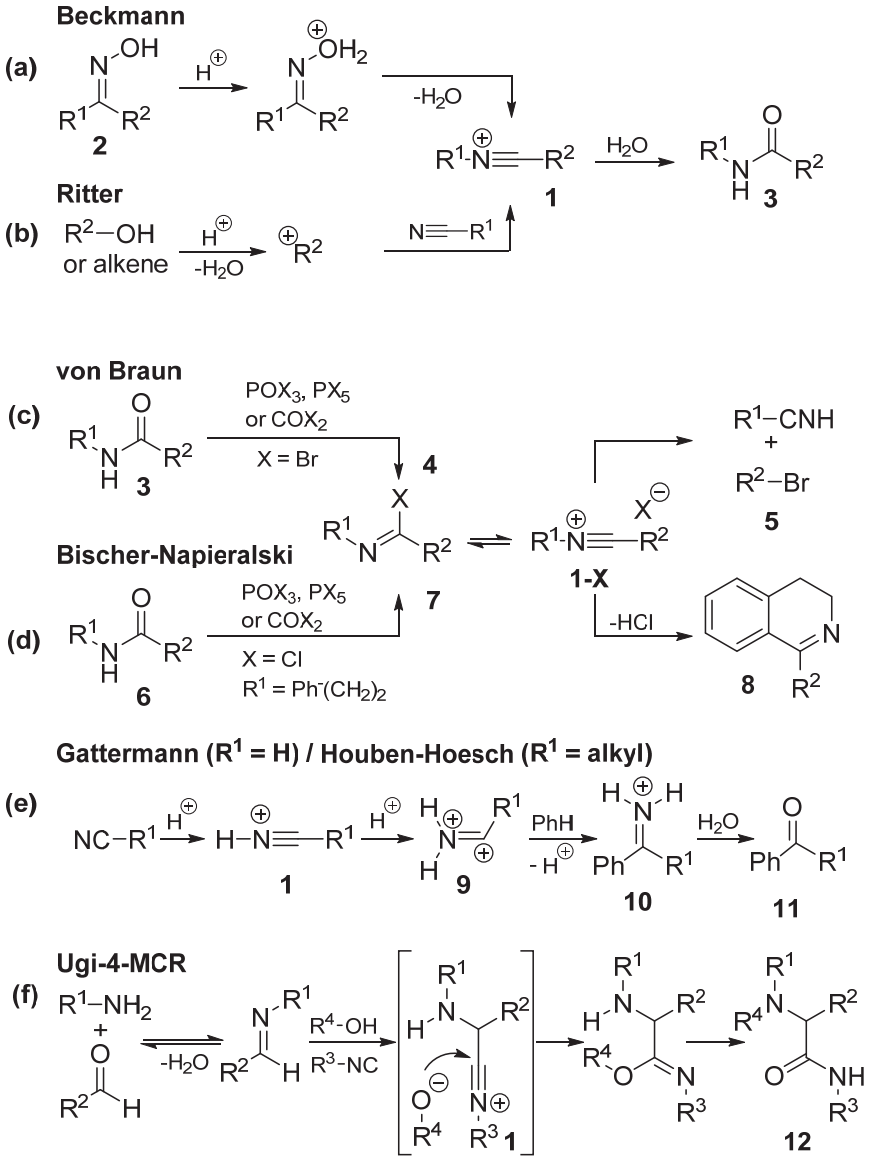
1.2 Nitrilium Ions

1.2.1 Reactive Intermediates

The best-known reaction in which the nitrilium ion plays a prominent role is the Beckmann rearrangement that converts oximes **2** into amides **3** (Scheme 1a). In this reaction, first reported in 1886,[2] the protonated oxime eliminates water to give a nitrilium ion that hydrolysis to an amide. In some cases the nitrilium ion intermediate has been observed spectroscopically[3] and even been isolated.[4] Amides are also formed by hydrolysis of nitrilium ions in the closely related Ritter reaction,[5] be it that they are obtained from a nitrile and an carbenium ion that is acid-generated from an alcohol or alkene (Scheme 1b).[6] Nitrilium ions are also intermediates in the von Braun reaction,[7] which instead concerns the degradation of an amide on treatment with a bromide source to give an alkyl bromide (Scheme 1c). The degradation starts by converting a secondary N-alkyl amide **3** into imidoyl bromide

4, which is in equilibrium with nitrilium bromide **1-Br**. The latter dissociates into a nitrile and a carbenium ion that reacts with the liberated bromide ion to give alkyl bromide **5**.[6c, 8] Another transformation involving the nitrilium ion is the Bischler-Napieralski reaction[9] that converts β-phenethylamides **6** into 3,4-dihydroisoquinolines **8** (Scheme 1d). In this reaction the amide is treated with a chloride to give an equilibrium mixture of imidoyl chloride **7** and nitrilium chloride **1-Cl** that undergoes a phenyl-induced ring closure,[6c, 10] but if the phenyl group is not nucleophilic enough, the nitrilium ion can expel a nitrile to give either β-phenethyl-chloride by the von Braun amide degradation or styrene by the retro-Ritter reaction.[6c, 10] Nitrilium ions have been implicated in the Gattermann[11] and Houben-Hoesch[12] reactions (Scheme 1e) in which aromatic compounds are formylated or acylated under acidic conditions with hydrogen cyanide or a nitrile, respectively;[13] even protonated nitrilium ion **9** (i.e., a dication) may be involved as the reaction with benzene occurs only in superacids.[14] Nitrilium ions are also known to be intermediates in the hydrolysis of imidoyl chlorides[15] and the acid catalyzed hydrolysis of isocyanides[16] and ketenimines.[17] Also the widely applied Ugi 4-component reaction[18] for the synthesis of α-amino acylamides **12**, but not the related Passerini reaction,[19] is considered to proceed through a nitrilium ion intermediate (Scheme 1f).[20]

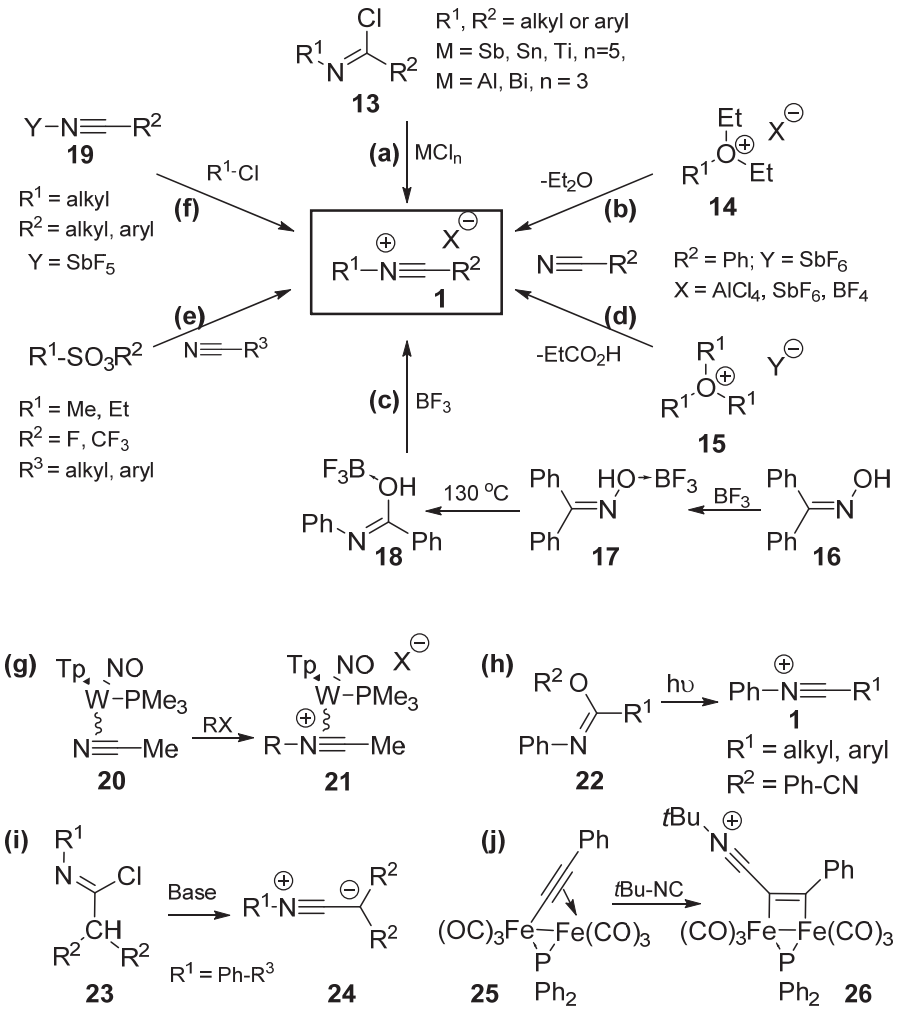
These examples amply illustrate the relevance of nitrilium ion intermediates in organic synthesis. This review goes beyond these established reactions to expand the scope of nitrilium ions as imine synthons for the synthesis of N-heterocycles and N,P-ligands that have their merits in coordination chemistry.



Scheme 1. Reactions involving nitrilium ion intermediates.

1.2.2. Stable Nitrilium Salts

Stable nitrilium salts are equally well established as the reactive intermediates that hydrolyze,[4a, 21] expel a nitrile, or undergo cyclization and are commonly generated from imidoyl halides or nitriles. Already in the 1950s, both Klages[22] and Meerwein[23] reported stable nitrilium salts by abstracting a Cl^- ion from imidoyl chlorides **13** with Lewis acids like $SbCl_6$, $SnCl_5$, $TiCl_5$, $AlCl_3$, $BiCl_3$, BCl_3[21c] and recently we applied TMSOTf successfully[24] (Scheme 2a). Imidoyl chlorides undergo first order dissociation in aqueous organic solvents to nitrilium ions, which, of course, hydrolize instantly to amides.[15] Meerwein was the first to show that nitriles can be N-alkylated with triethyloxonium-BF_4 (**14**), known as Meerwein's reagent, or its $SbCl_6^-$ and $AlCl_4^-$ derivatives (Scheme 2b).[23] He also showed the nitrilium ions to be involved in the Beckmann rearrangement by obtaining nitrilium-BF_4 salt **1** on heating the BF_3 adduct (**17**) of benzophenone oxime **16** and treating product **18** with additional BF_3 (Scheme 2c).[4c] Subsequently, stable nitrilium salts have been shown to result from N-alkylating acetonitrile and benzonitrile with reagents such as $HC(OEt)_2$+$SbCl_6^-$ (Scheme 2d),[25] the O-methyldibenzofuranium-BF_4 salt,[26] methyl triflate,[27] $MeSO_3F$,[28] and $EtSO_3F$ (Scheme 2e).[28b] N-alkylnitrilium salts are also formed on reacting alkyl halides with $FeCl_3$ or $SbCl_5$-coordinated nitriles **19**[23, 29] (Scheme 2f) and even by treating a CN-containing phosphaylid with Meerwein's salt,[30] while a μ^2-TpW(NO)(PMe_3) stabilized nitrilium ion (**21**) results from the correspondingly coordinated acetonitrile **20** (Scheme 2g), obtained in situ from the μ^2-benzene complex.[31]

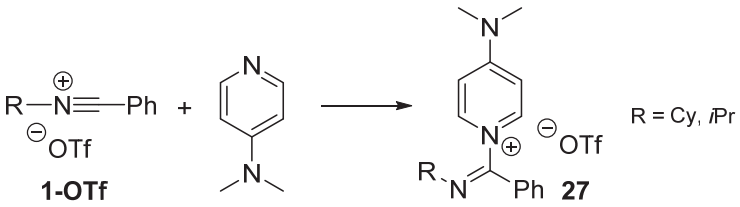


Scheme 2. Syntheses of stable nitrilium salt

Light-induced fragmentation is another method as illustrated for the formation of *N*-phenylnitrilium ion **1** by photocleavage of benzimidate ester **22** (Scheme 2h).[21a, 21b] Even nitrilium ylides, such as **24**, can be obtained by aqueous deprotonation of imidoyl chlorides **23** (Scheme 2i) and trapped by dipolarophiles like methyl

acrylate.[32] There are few cases of transition metal mediated syntheses of stable nitrilium ions, such as the nucleophilic attack of *t*-butylisocyanide on μ^2-η^2-acetylide diiron complex **25** to give ion **26** (Scheme 2j).[33] Similar reactions have been reported for the allenyl $[Fe_2(CO)_6(\mu\text{-}PPh_2)]$ complex[34] and Os_3- and Ru_3-complexes;[35] a related Fe_2-complexed nitrilium ion results from attack of *t*-butylisocyanide at $(Cp(CO)Fe)_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$.[36]

Recently we have shown that treating thermally labile *N*-alkyl nitrilium triflates with DMAP renders moderately air-stable adducts **27** (Scheme 3), which much improves the handling of the nitrilium ion while retaining their reactivity.[37] For instance, solid DMAP adduct **27** (R = *i*Pr) gave only 9% of the hydrolyzed product upon exposure to air for one month.



Scheme 3. Base stabilized nitrilium triflates

1.2.3. Structural Properties

Nitrilium ions have a linear conformation with an N≡C triple bond, implying a formally positively charged nitrogen atom. Illustrative are the three X-ray crystal structures shown in Figure 1.[24, 38] The average N≡C bond length of 1.135 Å for the nine nitrilium ions found in the Cambridge Structural Database[24, 30, 34-36, 38-39] compares well with the 1.131 Å of a nitrilium ylide,[40] the 1.138 Å of aryl nitriles,[41] and the 1.136 Å of alkyl nitriles[41]. The average C-N≡C and N≡C-C bond angles of 174.5° and 177.1°, respectively, reflect the near linearity of the ions. The IR stretch vibration observed for 21 nitrilium salts, carrying aryl and alkyl groups, ranges from

2300 to 2420 cm^{-1} and is fully in line with the N≡C triple bond character.[4a, 21c, 24, 27a, 42] The observed ^{13}C NMR chemical shifts of the -N≡*C*- carbon of 14 nitrilium ions[24, 28d, 29b, 43] range from 102.6 to 125.2 ppm and compare with the 116.4 ppm ($CDCl_3$) for acetonitrile;[44] *C*-alkyl nitrilium ions (108.6 – 125.2 ppm) are generally deshielded from the *C*-aryl substituted ones (102.6 – 107.7 ppm). The ions typically have $^1J(C,N)$ coupling constants of 42.1 to 50.0 Hz. Noteworthy is that the ^{14}N NMR resonance for $[Me\text{-}N{\equiv}C\text{-}Me]^+$ is 110 ppm deshielded from that of acetonitrile,[4a] reflecting the difference in N-coordination.

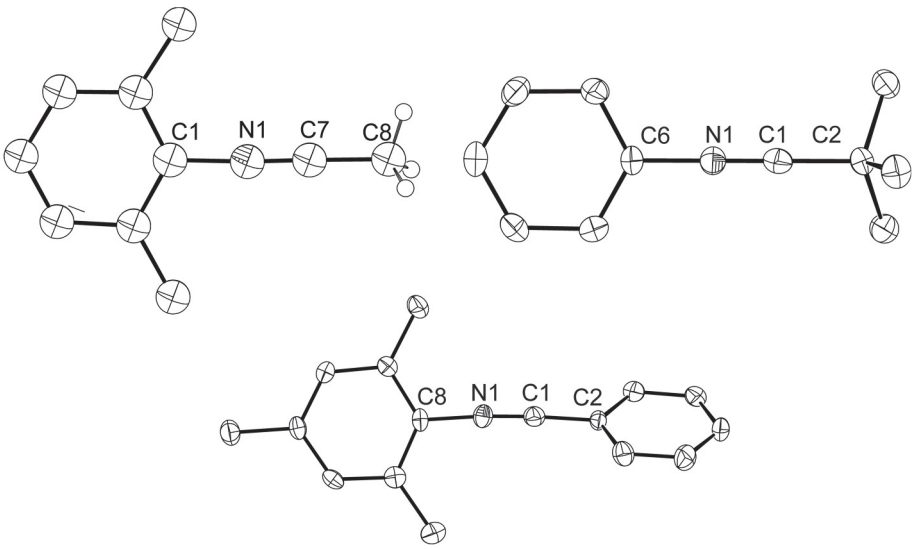
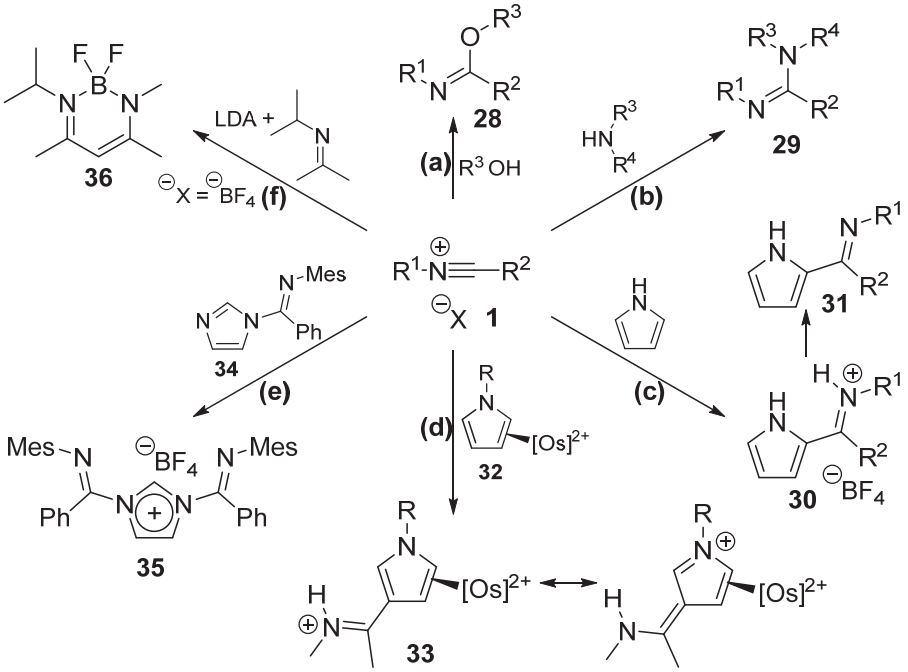


Figure 1. Molecular structures of the (*N*-2,6-dimethylphenyl)(methyl)carbonitrilium ion[38] (top-left), (*N*-phenyl)(*tert*-butyl)carbonitrilium ion[24] (top-right) and (*N*-2,4,6-trimethyl-phenyl)(phenyl)carbonitrilium ion[24] (bottom). Reported selected bond lengths (Å) and angles (deg) for top-left structure: N1-C7 1.132, C1-N1-C7 177.4, N1-C7-C8 179.2, for top-right structure: N1-C1 1.125(3), C1-N1-C6 179.3(2), N1-C1-C2 177.7(2), for bottom structure (second crystallographically independent structure between brackets): N1-C1 1.140(4) [1.142(4)], C1-N1-C8 176.1(3) [176.0(3)], N1-C1-C2 177.6(4) [174.8(3)].

1.3. Imine Synthons

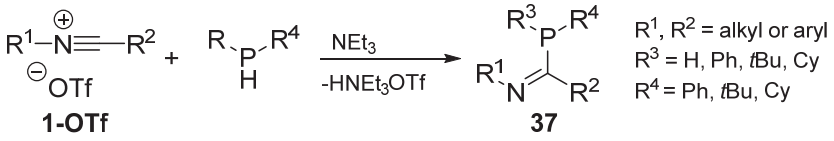
One of the early examples of using nitrilium salts to generate imines comes from Turrell *et al.*, who synthesized aminoester **28** from (*N*-phenyl)(phenyl)-**1-SbF_5** and phenol (Scheme 4a).[42] Treating *in situ* generated **1-BF_4** with alcohols also gives **28**, which on reduction ($NaBH_4$) converts readily into secondary amines.[45] Similarly, *N*-methyl-**1-OTf** reacts with alcohols to give **28** and forms thioamino-esters on using thiols.[27b] Recently, based on ^{1}H NMR ^5J(H,H) coupling constants,[46] it was concluded that the addition of methanol and ethanol to (*N*-methyl)(methyl)-**1-O_3SF** forms the expected *Z*-iminium ions, which on deprotonation isomerize to the *E*-imines.[28d] Such behavior was also reported for the nucleophilic attack of acetate to nitrilium ions, which showed the selective formation of *Z*-*N*-acyl-acetamides with subsequent slow isomerization to the *E*-isomer.[47] Likewise, reaction of an azide anion with nitrilium ions resulted selectively in *Z*-imidoylazides, which upon slow isomerization cyclized to the corresponding tetrazoles.[47] Other *O*-nucleophiles can also be used, such as olefin-bound η^2-acrolein osmium(II) complexes in which the carbonyl oxygen attacks the nitrilium ion, resulting in a η^3-vinyl osmium complex.[48]

Reaction of *N*-aryl-**1-$SbCl_6$**,[42] *N*-alkyl-**1-$FeCl_4$**,[49] and **1-OTf**,[27b] with primary or secondary amines gives amidines **29** upon deprotonation of the amidinium intermediate (Scheme 4b). The power of this method was demonstrated by Gordon *et al.* for the high-yield synthesis of otherwise inaccessible *N*-*tert*-butylamidines as precursors for bulky amidinate ligands.[50] Also carbon-based nucleophiles can be used as illustrated by the reaction of (*N*-methyl)(methyl)-**1-BF_4** with pyrrole (Scheme 4c) that gives a mixture of the iminium ion **30** and imine **31**; full conversion to **31** results on NaOH quenching. A study on the reactivity of pentaamineosmium(II)-η^2-pyrrole complex **32** revealed that the pyrrole group changes from the α to the β-position on addition of a nitrilium ion to give **33** (Scheme 4d).[51] A similar β-addition to nitrilium ions was shown for the analogues η^2-furan complexes.[52]



Scheme 4. Nitrilium salts as imine synthons

C-phenyl nitrilium salts **1-BF$_4$** reportedly react in high yield with imino-imidazoles **34** to bis-imino-imidazolium salt **35** (Scheme 4e) that are precursors for bis-imino *N*-heterocyclic carbenes, but the parent imidoyl chloride shows no reactivity.[53] (*N*-methyl)(methyl)-**1-BF$_4$** has been shown to react in THF with a lithiated *C*-methyl imine to generate in poor yield the BF_2-adduct of asymmetrically substituted β-diimine **36** (Scheme 4f).[54] Recently, we have shown that **1-OTf** can be used as an imine synthon for the high-yield synthesis of iminophosphanes **37**, which can function as either anionic phosphaamidinate ligands (for R^3 = H)[24] or as neutral 1,3-P,N-ligands (R^3, R^4 = Ph, *t*Bu or Cy)[55] for transition metal coordination (Scheme 5).

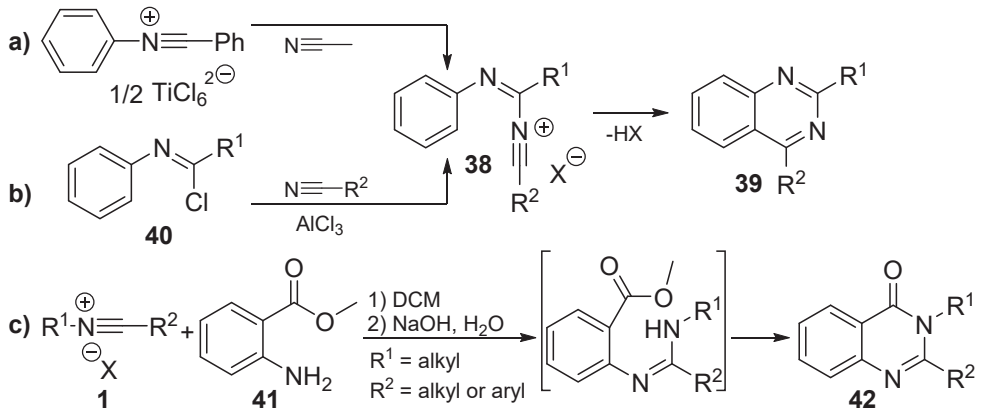


Scheme 5. synthesis of imino-phosphanes

1.4. Heterocycles

1.4.1 From Stable Nitrilium Ions

Various heterocyclic compounds have been synthesized by nucleophilic attack on a nitrilium ion followed by intramolecular cyclization. For instance, when nitriles were reacted with (*N*-phenyl)(phenyl)-**1-$(TiCl_6)_{0.5}$** (Scheme 6a) or *N*-phenyl-imidoylchloride **40**, using $AlCl_3$ for Cl-abstraction, the resulting intermediate **38** cyclized immediately to chinazoline **39** (Scheme 6b)[56] except when the *N*-phenyl group carried ortho-methyl substituents. The method has been used for the synthesis of 2-aminochinazolines (i.e., $R^1 = NR^3R^4$; R^3, R^4 = aryl or alkyl) by using $SnCl_4$ as Lewis acid.[57] A similar methodology is reportedly also suited for the synthesis of 3,4-dihydro-4-oxo-quinazoline **42** by *N*-nucleophilic attack of methylanthranilate **41** at *N*-alkyl-**1-$FeCl_4$**[58] or its triflate [27b] (Scheme 6c) as well as for imidazoles when propargylamine or α-aminoesters are used.[58]

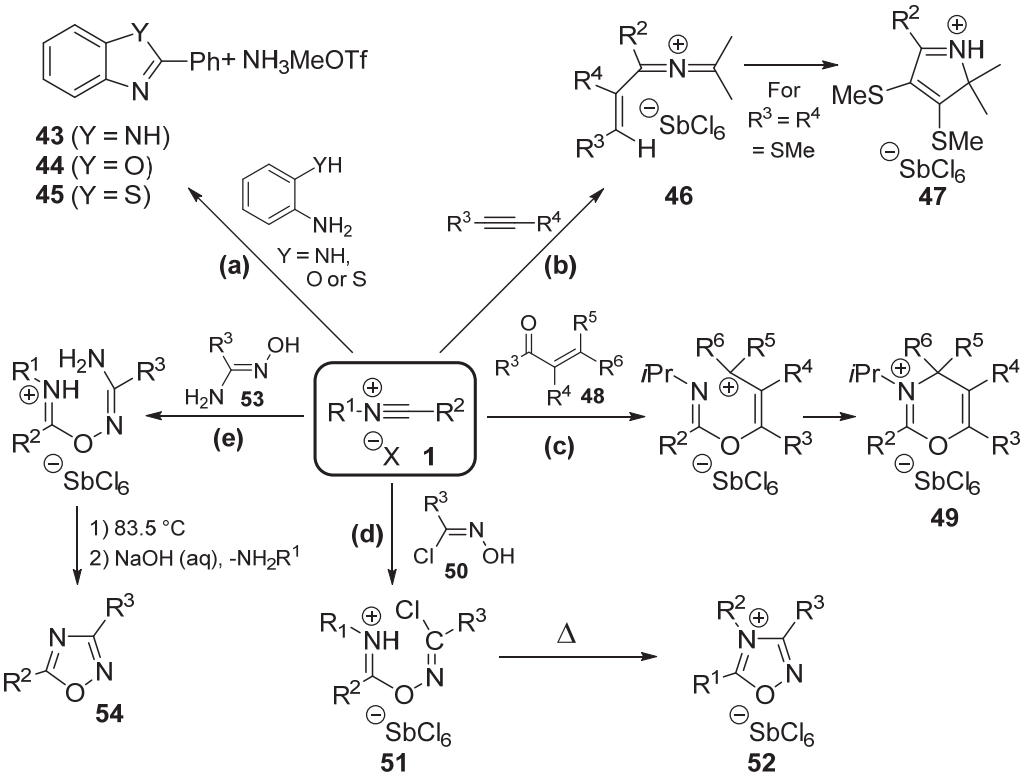


Scheme 6. Synthesis of chinazolines and 3,4-dihydro-4-oxo-quinazolines from nitrilium ions

*C*1-phenyl-substituted benzamidazole **43** were obtained from (*N*-methyl)(phenyl)-**1-OTf** and 2-aminoaniline with benzoxazole **44** and benzothiazole **45** resulting likewise from 2-aminophenol and 2-aminothiophenol, respectively (Scheme 7a);[13b] in the reaction affording **43**, the amine groups of 2-aminoaniline attack the nitrilium carbon atom sequentially with expulsion of methylammonium triflate. Reacting diaminomaleonitrile with (*N*-methyl)(methyl)-**1-OTf** afforded likewise 2-dimethyl-5-amino-4-(*C*-cyanoformimidoyl)imidazole and 6-carbamoylpurines on subsequent treatment with ketones.[59]

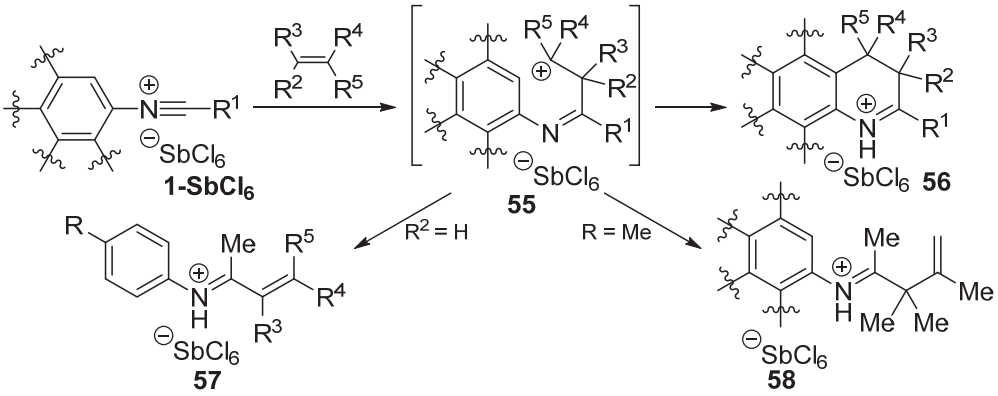
Reacting *N*-isopropyl-**1-SbCl$_6$** with acetylenes yielded 2-azoniaallenes **46** after a 1,5-H shift (Scheme 7b). When instead 1,2-bis(methylthio)acetylene was used a subsequent slow cyclization occurred to the 2*H*-pyrrolium salt **47**.[29b] A variety of 4*H*-1,3-oxazinium salts **49** were obtained from the reaction of *N*-alkyl-**1-SbCl$_6$** with chalcone **48a** (R^3,R^5 = Ph; R^4,R^6 = H), presumably by attack of the carbonyl oxygen to the nitrilium salt followed by *N*-nucleophilic attack at the resulting carbocation (Scheme 7c).[60] 6*H*-1,3-oxazinium salts resulted instead with α,β-unsaturated aldehydes (**48b**, R^3 = H), presumably via an initial [2+2]-cycloaddition of the aldehyde

and the nitrilium ion followed by ring opening and cyclization by *O*-nucleophilic attack. 3,4,5-Trisubstituted 1,2,4-oxadiazolium salts **52** resulted from *O*-nucleophilic attack of *N*-hydroxycarboximidoyl chloride **50** to *N*-alkyl-**1-SbCl$_6$** and heat induced cyclization of intermediate **51** (Scheme 7d);[61] **52** resulted in a single step at room temperature on using nitrile oxides instead of **50**. Similarly, amide oximes **53** were shown to react with both *N*-alkyl- and *N*-aryl-**1-SbCl$_4$** to give 3,4,5-trisubstituted 1,2,4-oxadiazoles **54** upon basic work-up and expulsion of an amine (Scheme 7e).[62]



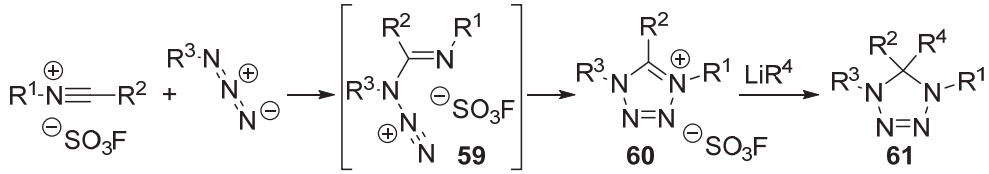
Scheme 7. Heterocycle synthesis from nitrilium ions

N-aryl-**1-SbCl$_6$** reportedly reacts with alkenes to yield 3,4-dihydroquinolinium salts **56** (Scheme 8).[63] The reaction was postulated to proceed by electrophilic attack of the nitrilium ion to the alkene to give intermediate **55**, followed by intramolecular electrophilic aromatic substitution. Support for **55** came from the isolation of Houben-Hoesch product **57** and formation of the ene-reaction product **58**. Similarly, electron rich acetylenes were shown to provide quinolones.[64]



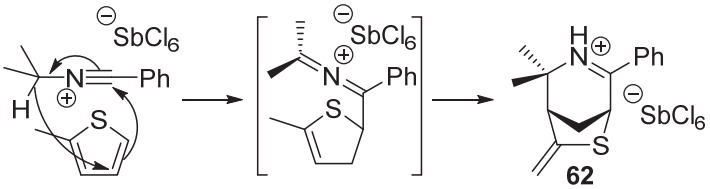
Scheme 8. 3,4-Dihydroquinolinium salts synthesis from N-aryl nitrilium ions and alkenes

1,4,5-Tetrazolium salts **60** were stereoselectively formed on reacting azides with **1-SO$_3$F** (Scheme 9).[65] *N*-nucleophilic attack of azides to the nitrilium ion gives intermediate **59**, which cyclizes to 1,4,5-tetrazolium salt **60.** This salt can be converted to the tetrazoline **61** by reduction with $LiBH_4$ or reaction with organolithium reagents.



Scheme 9. The reaction of nitrilium ions with azides

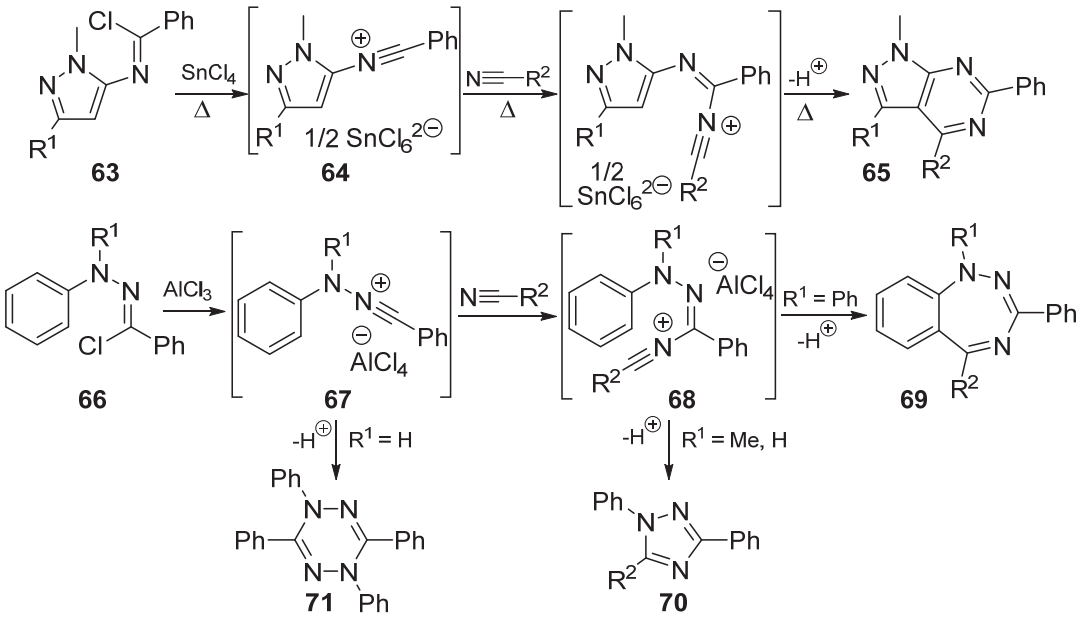
The reaction between *N*-*iso*-propyl-**1-SbCl$_6$** and 2-methylthiophene affording hetero-bicyclic **62** (Scheme 10) was postulated to proceed by an intermolecular ene-reaction followed by cyclization through electrophilic attack on the heterocyclic double bond and subsequent tautomerization, albeit that the last step may also proceed by means of a concerted 6-(3,5)-ene cyclization.[29a]



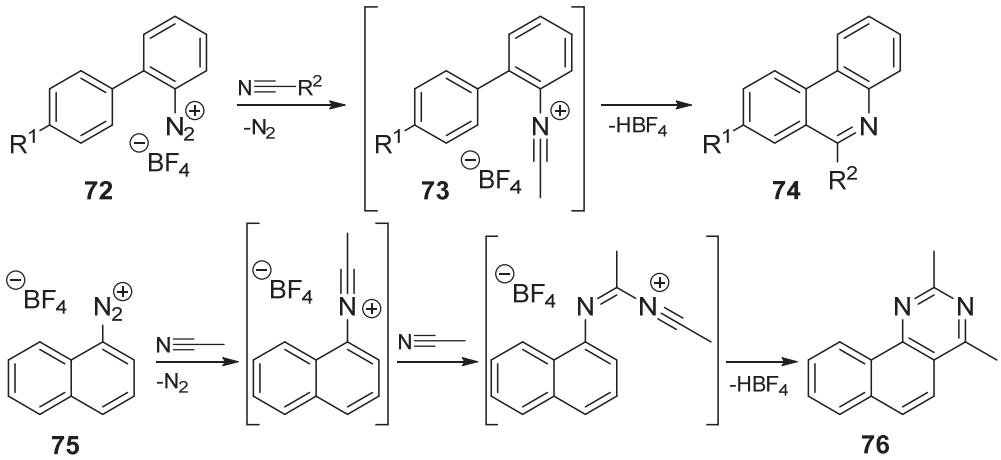
Scheme 10. Ene reactions with nitrilium ions.

1.4.2. From in situ Generated Nitrilium Ions

Heterocyclic compounds are equally well accessible by means of *in situ* generated nitrilium ions that undergo an intramolecular cyclization. Exemplary is the synthesis of pyrazolo[3,4-*d*]pyrimidines **65** by treating C5-substituted *N*-pyrazolyl imidoyl chlorides **63** with $SnCl_4$ in the presence of nitriles (Scheme 11, top), which proceeds analogous to the discussed synthesis of chinazolines (Scheme 6; top); nitrilium ion **64**, generated by Lewis acid induced Cl-abstraction, reacts with the nitrile to subsequently undergo cyclization by intramolecular electrophilic aromatic substitution.[66] Likewise, hydrazine based imidoylchlorides **66** have been converted to *1H*-1,2,4-benzotriazepines **69**, but the reaction is sensitive to the hydrazine *N*-substituent (Scheme 11, bottom).[67] Whereas **69** was formed when this substituent is a *N*-phenyl group, this is not the case with the *N*-methyl derivatives that gave instead 1,2,4-triazoles **70**, apparently by the preferred electrophilic attack at the amine of intermediate **68**. In the absence of an *N*-substituent, **66** also reacted to triazole **71** besides the deprotonated dimer of nitrilium ion **67**.[68]

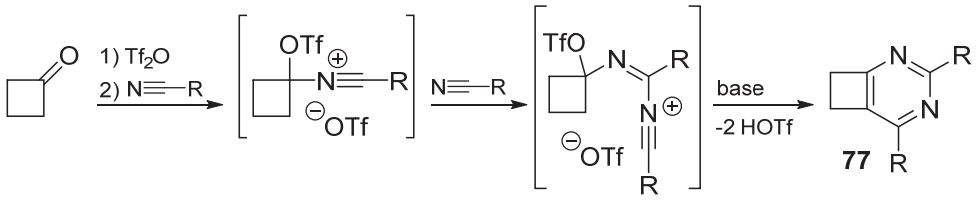


Scheme 11. Synthesis of pyrazolo[3,4-d]pyrimidines (top) and 1H-1,2,4-benzotriazepines and 1,2,4-triazoles (bottom)



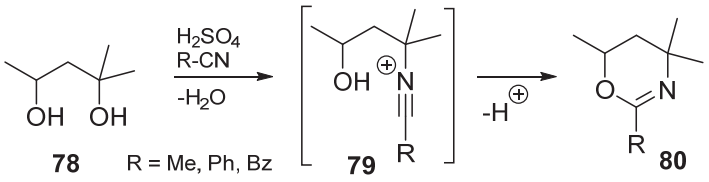
Scheme 12. Phenanthridine synthesis from diaryldiazonium salts and nitriles

The biaryldiazonium-BF_4 salts **72** react with nitriles under expulsion of N_2 to give **73** as intermediates, which undergo an intermolecular electrophilic aromatic substitution to phenanthridines **74** (Scheme 12, top) that are tedious to isolate and are therefore often converted to picrates.[69] Interestingly, the nitrilium ion resulting from the reaction of 1-naphthalenediazonium-BF_4 (**75**) with acetonitrile didn't cyclize to 2-methylbenzo[*c,d*]indole, but reacted instead with another acetonitrile molecule to cyclize to 2,4-dimethylbenzo[*h*]quinazoline (**76**; Scheme 12, bottom);[69] the reaction resembles Meerwein's chinazoline synthesis shown in Scheme 6. Similar reactivity with the double uptake of a nitrile was found in the reaction with cyclobutanone when treated with triflic anhydride giving cyclobutapyrimidines **77** as product (Scheme 13).[70]



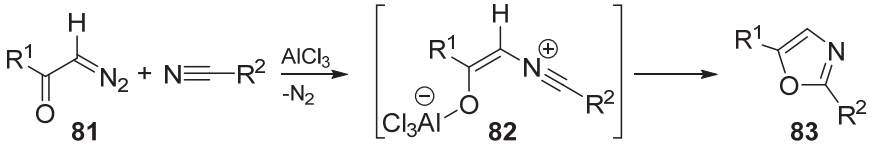
Scheme 13: Synthesis of cyclobutapyrimidines

Heterocycles can also be generated in a Ritter-like reaction in which the nitrilium ion, generated *in situ* from a carbocation and a nitrile, undergoes intramolecular cyclization. Illustrative is the synthesis of dihydro-1,3-oxazine **80** from diol **78**, which proceeds by generating an incipient carbocation that reacts with a nitrile to generate the transient nitrilium ion intermediate **79** (Scheme 14).[71] A similar reaction occurred with a dinitrile succinonitrile as only one nitrile reacted to the dihydro-1,3-oxazine with a pendant nitrile group.[72] Ritter-like reactions can also be used for the synthesis of 2-thiazolines,[73] 5,6-dihydro-1,3-thiazines,[73] and non-nitrile functionalized dihydro-1,3-oxazines.[74]



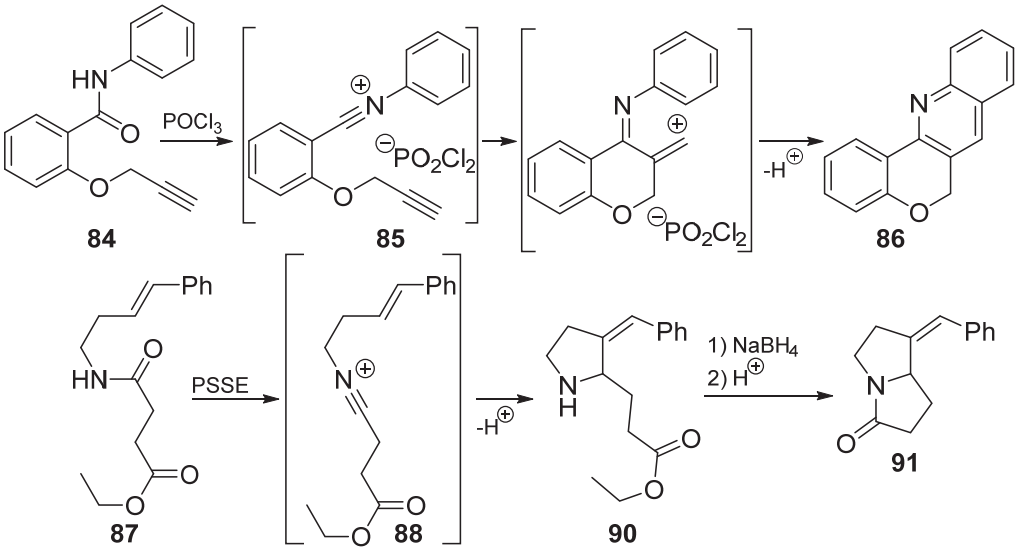
Scheme 14. Ritter like synthesis of dihydro-1,3-oxazines.

Diazocarbonyls **81** have been reacted with nitriles in presence of $AlCl_3$ to give oxazoles **83**,[75] which was postulated to be formed via intermediate **82** that undergoes intramolecular cyclization by *O*-nucleophilic attack (Scheme 15). However, executing the reaction with less than 2 equivalents of $AlCl_3$ generated α-chlorocarbonyl as byproduct, which could be prevented by using BF_3 instead.[76]



Scheme 15. Lewis acid promoted reaction of diazocarbonyls and nitriles

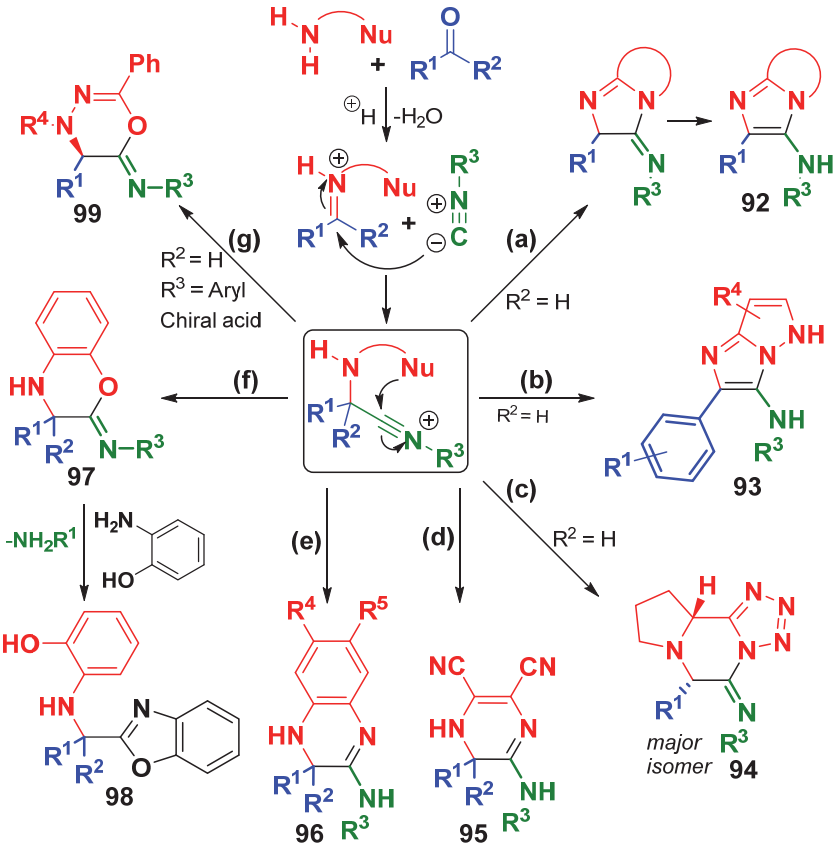
In situ generation of nitrilium ion **85** from amide **84** and $POCl_3$ was shown to lead to a cascade reaction resulting in 6*H*-[1]benzopyrano[4,3-*b*]quinolone **86** (Scheme 16; top).[77] Similarly, generating ion **88** from amide **87** and trimethylsilylpolyphosphate (PPSE) led directly to pyrroline ester **90** by electrophilic attack of the nitrilium carbon on the olefin.[78] Reduction of **90** with $NaBH_4$ initiates a second cyclization to give benzylidinepyrolizidone **91** (Scheme 16; bottom).



Scheme 16. Nitrilium ion generation from amides

Whereas the extensively reviewed Ugi reaction[18c, 20a, 20b, 79] (Scheme 1f) is beyond the scope of the present review, there are Ugi-like reactions involving a nitrilium ion intermediate with subsequent cyclization to a heterocycle, i.e., by intramolecular nucleophilic attack of the isocyanide at the ion center (Scheme 17). Typically, the nucleophile is part of the amine reactant (H_2N^Nu), as is the case for the reactions of 2-aminopyridine, 2-aminopyrimidine, and other heterocyclic amidines that render bicyclic 3-aminoimidazoles **92** (Scheme 17a).[80] Also pyrazole amidines have been shown to react in a 3-component reaction with benzaldehydes and isocyanides to give 3-aminoimidazoles **93** (Scheme 17b).[81] Asymmetric pyrazole tetrazole derivatives have been employed to synthesize heterocycles **94** (Scheme 17c).[82] The intramolecular nucleophile can also be another amine group, as was shown for the reaction of 2,3-diaminomaleonitrile with ketones and isocyanides to afford heterocycle **95** (Scheme 17d);[83] the reaction of ethylenediamine[84] with aldehydes and isocyanides yields similar results. Reaction of *o*-phenyldiamine with ketones (R^1,

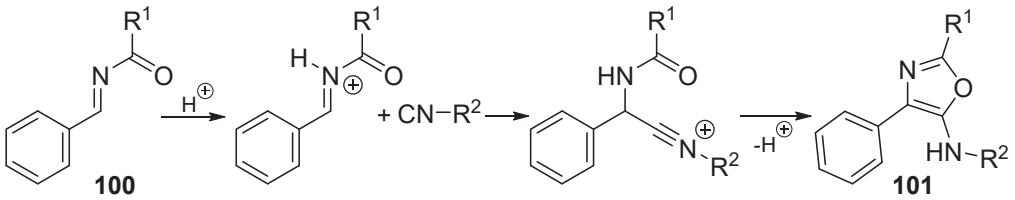
R^2 = alkyl) and isocyanides gave 3,4-dihydroquinoxalin-2-amines **96** (Scheme 17e);[85] on using aldehydes (R^2 = H), **96** could be converted to quinoxaline on oxidation with DDQ.[86]



Scheme 17. Isocyanide based heterocycle syntheses through nitrilium ion trapping

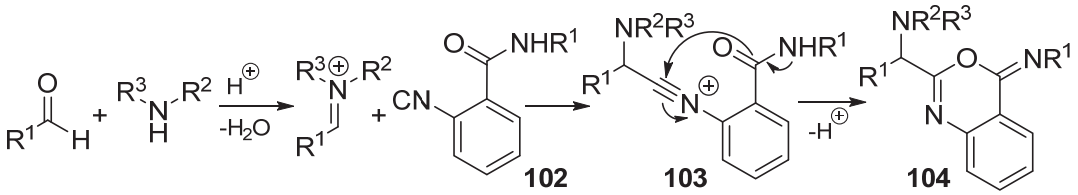
Oxygen nucleophiles can also be used, as has been shown for the reaction of 2-aminophenol, the cyclic ketone *N*-methyl-4-piperidone, and isocyanides that afforded bicyclic **97** (Scheme 17f).[87] A subsequent reaction with another molecule

of 2-aminophenol led to double addition at the imine carbon of **97** to give benzoxazoles **98** on expulsion of R^3-NH_2. With aldehydes (R^2 = H) instead of ketones, tautomerization of **97** occurred to 4*H*-benzo[1,4]oxazin-2-amines;[88] oxidation with DDQ gave 2*H*-benzo[1,4]oxazin-2-imines.[89] *N*'-benzylbenzo-hydrazide reportedly gives heterocycle **99** (Scheme 17g) in high *ee* in the presence of a catalytic amount of a chiral acid, such as 3,3' substituted (R)-binaphthalenyl-2,2'-dicarboxylic acid derivatives, which transfers its chiral information as counter ion.[90] An alternative route to *C,N*-cyclic heterocycles **99** is the synthesis directly from *C,N*-cyclic *N*'-acyl azomethine imines and isonitriles.[91] Similarly, imine **100** was shown to react with isocyanides under acidic conditions to give aminooxazoles **101** (Scheme 18).[92]



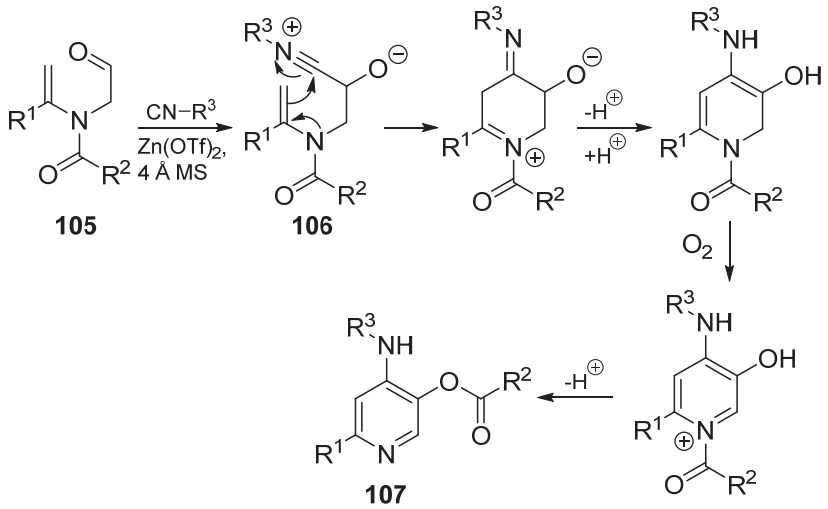
Scheme 18. Synthesis of aminooxazoles **100** from imine **101** and isocyanides

The nucleophile in the intramolecular reaction does not need to be part of the amine component, as was demonstrated for 2-isocyanobenzamide (**102**) with its amide oxygen attacking the nitrilium carbon of intermediate **103** to give 4-imino-*4H*-3,1-benzoxazines **104** (Scheme 19).[93]



Scheme 19. Synthesis of 4-imino-*4H*-3,1-benzoxazines **104**

Nucleophilic attack of isocyanides on N-formyl,methyl-substituted enamides **105** gave nitrilium ylide **106**, which after tautomerization and oxidation with molecular oxygen, underwent an intermolecular acyl transfer from nitrogen to oxygen, to afford the pyridine derivatives **107** (Scheme 20).[94]



Scheme 20. Synthesis of pyridines **107**

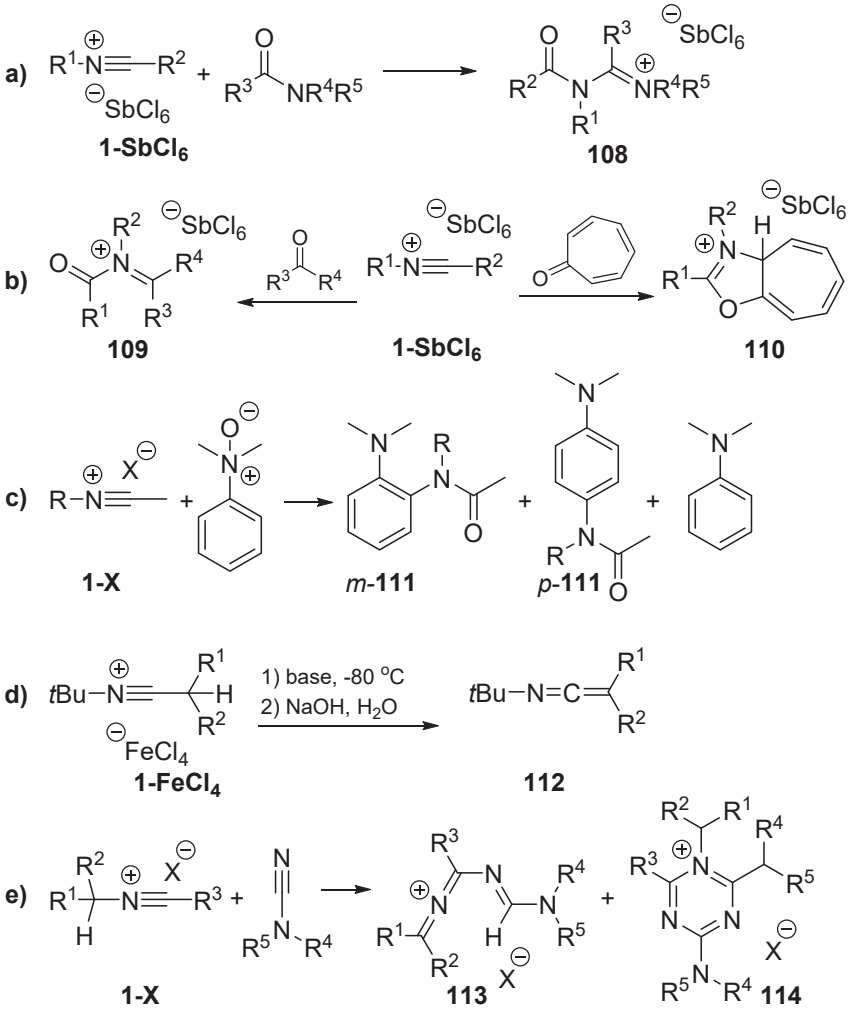
1.5. Miscellaneous Reactions

The reaction of nitrilium salts with a range of amides has been studied. Whereas tertiary amides gave *N*-acylamidinium salts **108** as the sole product (Scheme 21a),[43a] isomeric mixtures were obtained with secondary amides.[95] Reacting **1-$SbCl_6$** with a range ketones resulted in the insertion of the nitrilium ion to give **109** (Scheme 21b, left),[43b] except for tropone that gave instead cycloaddition product **110** (Scheme 21b; right),[96] presumably by attack of the oxygen on the nitrilium carbon followed by cyclization.

When *N,N*-dimethylaniline oxide was reacted with *C*-methyl-**1**-**X** a mixture of *ortho*- and *para*-*N,N*-dimethylaniline acetamides **111** and *N,N*-dimethylaniline was obtained (Scheme 21c), likely by *O*-nucleophilic attack on the nitrilium ion followed by the dissociation and recombination of the AcN-R fragment.[28c] Nitrilium ions **1-$FeCl_4$** with an α-hydrogen on the *C*-substituent can be deprotonated at -80 °C to ketene imines **112** (Scheme 21d),[97] but di- or trimerization occurs at higher reaction temperatures.

Non-interconverting azoniaallenes, $R_2C{=}N^+{=}CR{-}N{=}CH{-}NR_2$ (**113**), and triazinium salts **114** have reportedly been formed on reacting aminonitriles with nitrilium ions that carry an *N*-α-hydrogen (Scheme 21e).[98] The azoniaallenes were postulated to be formed by an ene reaction, while the triazinium salts were considered to be the product of a concerted or stepwise [2+2+2] cycloaddition.

Nitriles can be reduced to aldehydes by means of a nitrilium ion strategy. The nitriles are first converted to *N*-isopropyl-**1**-**$FeCl_4$** by treatment with $FeCl_3$ and isopropylchloride, followed by reduction with triethylsilane to imines and subsequent hydrolysis to aldehydes.[99] The method is suited for a wide range of alkyl and aryl nitriles and gives aldehydes in nearly quantitative yields.



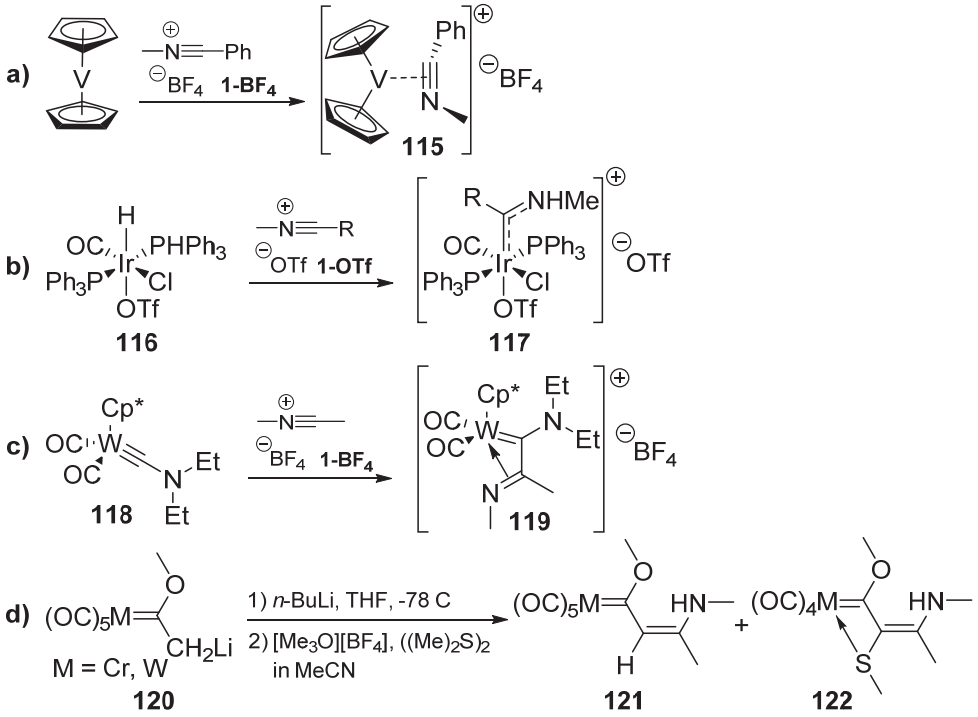
Scheme 21. Miscellaneous reactions with nitrilium ions.

1.6. Reactions with Transition Metal Complexes

Nitrilium ions coordinate to transition metals in a manner similar to the isoelectronic and isostructural acetylenes. Exemplary is the η^2-coordination of (*N*-methyl)(phenyl)-**1-BF$_4$** to vanadocene (**115** Scheme 22a).[100] Similar η^2-nitrilium complexes have been reported for TpW(NO)(PMe$_3$), which were synthesized by alkylating the nitrile complexes (Scheme 2g).[31] Nitrilium Ir-carbene complexes **117** can be accessed by reacting iridium(III) hydride complex **116** with various *N*-methyl-**1-OTf** (Scheme 22b).[101]

Nitrilium ions can react by means of a formal [2+2] cycloaddition with a W≡C triple bond as in tungsten complex **118** to form imino-carbene complex **119**; the molecular structure showed the imino-carbene unit to be η^3-coordinated to the transition metal (Scheme 22c).[102]

Treatment of deprotonated complex **120** (M = Cr, W) with the MeS$^+$-reagent [(CH$_3$)$_2$(CH$_3$S)S][BF$_4$], generated *in situ* in acetonitrile from dimethyl disulfide and Meerwein's reagent, showed the formation of both **121** and **122** (Scheme 22d) and evidently involves the incorporation of an iminium ion.[103] This ion likely results from *in situ* formation of a nitrilium ion by methylation with Meerwein's reagent of acetonitrile. Thioalkylation of the tautomer of **121** is assumed to give **122**, which showed coordination of the thio group to the metal center.



Scheme 22. Reactions of nitrilium ions with transition metal complexes

1.7. Conclusion and Perspectives

Stable nitrilium ions can be isolated and readily synthesized, commonly by alkylation of nitriles or Lewis acid abstraction of a chloride from imidoyl chlorides. Generally, $SbCl_6^-$ has been employed as counter ion, although for instance metal halides, BF_4, fluorosulfate or triflate have also been used. A wide range of unsaturated nitrogen containing heterocycles can be accessed from both stable nitrilium ions or by generating the nitrilium ion *in situ*, typically forming the heterocycle upon intramolecular electrophilic attack on the nitrilium- or iminium carbon of the formed intermediate. Furthermore, as will be shown in this thesis,

nitrilium ions are highly suitable imine synthons that react with a wide variety of nucleophiles.

1.8. Outline of this thesis

As was shown in this chapter, nitrilium ions are diverse building blocks for various applications. However, little recent applications have appeared in the literature. In this thesis, the use of readily prepared nitrilium triflates as imine synthons in the synthesis of a novel class of 1,3-iminophosphanes will be highlighted.

Chapter 2 describes the facile synthesis of phospha-amidines and phospha-amidinates using nitrilium triflates as imine synthon, allowing variation control of all substituents. Next to the synthesis of these 1,3-P,N-ligands, their coordination behavior is described. In **chapter 3** this strategy is expanded to the synthesis and coordination chemistry of 1,3-iminophosphanes, while supporting the obtained results with DFT calculations. In **chapter 4** the sensitive nature of nitrilium ions is addressed. Herein we describe the reaction of thermally labile nitrilium ions with weakly nucleophilic bases such as pyridine or 4-dimethylaminopyridine to stabilize them toward thermal decomposition while also decreasing the moisture sensitivity. In **chapter 5**, we extend our work on 1,3-P,N-ligands and elaborate on the synthesis of N,P,N-ligands including an efficient one-pot procedure, explore their coordination chemistry and report on their rearrangement to an unprecedented 1,3,5-phosphadiazapentadiene.

1.9. References and Notes

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